GLUTARALDEHYDE RETANNAGE OF CHROME LEATHER. EFFECT OF AMBIENT STORAGE ON SELECTED PROPERTIES OF THE LEATHER

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INTRODUCTION

Our previous studies amply demonstrated the valuable properties that glutaraldehyde imparted to leather, especially when used in combination with chrome in the tanning of hides and skins (1–7). One of the properties imparted to leather by glutaraldehyde was a markedly improved resistance to perspiration (2). This was true whether glutaraldehyde was used as the only tanning agent or in combination with chrome or other conventional tanning agents (1–7). We found that glutaraldehyde was used to its best advantage following chrome tanning of leather, since many tanners sort in the blue. However, our previous publications have also shown that applying the glutaraldehyde before, or even simultaneously with, the chrome was at least equally effective.

In one of our earlier studies (5) we investigated the effect of elevated temperatures on glutaraldehyde retannage of chrome-tanned sides. In that study the temperature was initially 63°C. and ended at 47°C. As expected, the effect of elevated temperature was to increase the rate of uptake of glutaraldehyde by the chrome-tanned side leather.

We now report the results obtained using chrome-tanned cabretta skins in a thermostatted Meissner mill. Because many post-tanning processes, such as retannage, coloring, and fat liquoring, are carried out at about 50°C., we chose this temperature for our studies on retannage of chrome leather with glutaraldehyde. The objective of this study was to determine the quantity of glutaraldehyde and the time of retannage required to attain perspiration-resistance in the chrome leather.

EXPERIMENTAL

Substrates

Table-run cabretta skins "in the blue" were obtained from a commercial tannery. After a brief washing in tap water, these were wrung and then stored in a large polyethylene bag in a refrigerator. A sample was clipped from each skin. These combined samples were oven-dried to estimate the water content of the wrung skins. Two skins, not retanned, were set aside as controls for perspiration resistance and shrinkage temperature (T_s).

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Tannage

All tannages were run at 50°C. No adjustment was made in the pH of the skins and no neutral salts were used. Skins were preheated by immersing them, in a sealed plastic bag, in hot running tap water. Preheating the water used in the 100 percent float and thermostatting an enclosed Meissner mill insured temperature control. The tannage was run for two or four hours using three levels of glutaraldehyde, namely, two, four, and eight percent of the 25 percent aqueous solution on the wrung blue weight (WBW). Aldehyde content of the float at the end of each run was determined by our usual iodometric procedure (8). Since the total water content of the system and the amount of aldehyde offered were known, the utilization could be readily calculated. The data are summarized in Table I.

TABLE I

EFFECT OF STORAGE TIME ON SELECTED PROPERTIES OF GLUTARALDEHYDE RETANNED CHROME SKINS

Glutaraldehyde Treated Chrome Skins		Change in Properties			
		T_s °C.			Perspiration Resistance
Retannage*	Uptake*	0 Months†	5 Months	14 Months	5 Months‡
2% for 2 hours	1.8%	97	88	77	0
2% for 4 hours	1.9%	97	89	79	1
4% for 2 hours	3.0%	97	90	79	1
4% for 4 hours	3.4%	97	86	80	2
8% for 2 hours	5.3%	96	88	76	1
8% for 4 hours	5.8%	98	89	76	2
Chrome control	None	93	84	71	0

*Percentages are based on the wrung blue weights using 25 percent commercial glutaraldehyde solutions.

†The time "0 Months" refers to the point of time after retannage, but before processing into finished leather. The "5 Months" and "14 Months" data are after finishing and storing under ambient conditions.

‡The number of cycles passed by a single specimen before failure. All except the control passed at "0 Months."

Two skins were retanned under each set of conditions, and after washing and draining were stored in plastic bags in a refrigerator. A strip was removed at the butt end from backbone to belly, for perspiration and T_s tests, before processing into finished leather. After all retannages were completed, 0.1 percent preservative was used to treat all skins to prevent possible mold growth. These were then processed along with a tannery's regular pack into finished garment leather.

Shrink Temperatures

Specimens were cut with a 7/32 x 2¼ in. die and were freely suspended in

a holder of our own design (9). Shrinkage temperatures were obtained shortly after retannage, and after storing the finished skins under ambient conditions for five months and again after 14 months. These data are presented in Table I.

Perspiration Resistance

A modified Colin-Russ (10) test was used to determine perspiration resistance. Samples for this test were cut out of the leather with the aid of a brass template (5.97 cm x 4.98 cm). The area change of the samples after the test was used as a criterion in judging which specimens passed. Surviving specimens, which showed area shrinkage of less than 15 percent, were submitted to a second and even third cycle of testing. Since all specimens, except the controls, passed the test immediately after processing, all were retested after five months of storage under ambient conditions and these data are given in Table I. Specimens were judged to have passed the test if little or no area loss was observed and if they also retained a good handle.

DISCUSSSION

The results of the perspiration test, both before and after commercial finishing, were consistent with past experience for chrome-tanned garment leather; the controls (those only chrome-tanned) failed and the glutaraldehyde retanned skins passed (2). The finished leathers were then stored under ambient laboratory conditions for five months and retested through as many as three cycles, except that the controls that failed previously were not included. The authors recognize that ambient storage in our laboratory is probably not the same as ambient storage in commerce. A reasonably consistent pattern emerged from these recycled test pieces; increasing the amount of glutaraldehyde offered for two hours increased the perspiration resistance as well as the actual amount of aldehyde bound (Table 1).

This table also shows that offering the same glutaraldehyde percentages for four hours gives an even greater increase in both the amount of glutaraldehyde bound and in the perspiration resistance as measured by the number of cycles of the perspiration test. Only those skins tanned with four percent or eight percent glutaraldehyde for four hours passed the second cycle of the perspiration test, and even these exhibited some area loss, although remaining flexible, at the end of the third and final cycle.

The shrinkage temperature was also monitored, but for a somewhat longer time period. After finishing, all pieces showed a continual lowering of shrinkage temperature until the termination of the experiment at 14 months' ambient storage. Glutaraldehyde retanned pieces had a final T_s value of 5° to 9°C. higher than the control. The number of degrees that the shrink temperature dropped on aging was very similar in all cases, but since the glutaraldehyde-retanned pieces started at a higher value, they also ended at a higher value when compared

to the control. The reason for the lowering of perspiration resistance and shrinkage temperature on aging is probably not related to the pH. At the end of retanning the pH was 4.0 to 4.3 and reached only 4.6 for the stored processed leather after five months of storage. A probable explanation for this drop in T_s is more likely a complex interaction of the tanned material with the particular fatliquor used rather than a failure of the tannage itself.

In summary, the data show that even the minimum retannage of two percent of the 25 percent glutaraldehyde solution for two hours at 50°C. gave perspiration resistance when tested immediately after processing. However, to retain perspiration resistance five months later, at least two percent for four hours or four percent for two hours was needed. Increasing the time of retannage to four hours and using either four percent or eight percent of the glutaraldehyde solution enabled the sample to survive two cycles in the modified Colin-Russ test and thus resulted in improved perspiration resistance. The data in Table I suggest that it is not only the amount of glutaraldehyde taken up by the skin, but also the time of reaction and concentration of glutaraldehyde that influence the degree and endurance of perspiration resistance in the skins used in this study.

REFERENCES

1. Fein, M. L., Harris, E. H., Jr., Naghski, J., and Filachione, E. M. *JALCA,* **54,** 488 (1959).
2. Filachione, E. M., Fein, M. L., Harris, E. H., Jr., Luvisi, F. P., Korn, A. H., Windus, W., and Naghski, J. *JALCA,* **54,** 668 (1959).
3. Fein, M. L., Filachione, E. M., Naghski, J., and Harris, E. H., Jr. *JALCA,* **58,** 202 (1963).
4. Filachione, E. M., Fein, M. L., and Harris, E. H., Jr. *JALCA,* **59,** 281 (1964).
5. Filachione, E. M., Fein, M. L., and Harris, E. H., Jr. *JALCA,* **59,** 378 (1964).
6. Happich, M. L., Naghski, J., and Windus, W. *JALCA,* **63,** 74 (1968).
7. Luvisi, F. P., and Filachione, E. M. *JALCA,* **63,** 584 (1968).
8. Fein, M. L., and Harris, E. H., Jr. U. S. Agricultural Research Service, ARS-73-37, November, 1962.
9. Fein, M. L., Harris, E. H., Jr., Calhoun, R. R., Jr., and Boyd, J. N. *JALCA,* **60,** 15 (1965).
10. Happich, W. F., and Windus, W. *JALCA,* **58,** 646 (1963).